Contents lists available at ScienceDirect

## Renewable and Sustainable Energy Reviews

journal homepage: www.elsevier.com/locate/rser



### Decarbonization of fossil fuels as a strategy to control global warming

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#### ARTICLE INFO

### Article history: Received 25 April 2010 Accepted 22 November 2010

#### ABSTRACT

With the world reaching near-total consensus on the seriousness of the global warming impacts, and on the urgency to halt further warming, R & D efforts have intensified many-fold to find ways and means of global warming control. One of the avenues being explored is 'decarbonization' of fossil fuel use by either decarbonizing the fuels before they are burnt or by capturing the CO<sub>2</sub> they emit on combustion.

In this paper the various available options are reviewed in the context of their economic and environmental viability. It emerges that even as the goal is very enchanting, the possibility of it's realization appears remote. It also follows that the only sure method of reducing greenhouse gas emissions presently available to humankind is by reducing consumption of energy and other resources.

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### 1. Introduction

If ways and means can be found to 'capture' CO2 which is released during the use of fossil fuels, further global warming can be halted. Or if fossil fuels can be decarbonized before they are burnt, by recovering solid carbon from them, the same objective can be achieved. It will also give the world atleast 200 more years to fully shift to alternative energy sources because CO2 capture will enable the use of the existing reserves of fossil fuels (which are expected to last 200 years) without the risk of worsening global warming that has already occurred.

And if ways can be found to capture the CO<sub>2</sub> that has already been released into the atmosphere? That would be absolutely fantastic because then we can reverse global warming and bring our ailing earth (with is getting increasingly 'feverish') back to

These are enchanting prospects. But, as of now neither carbon nor CO<sub>2</sub> capture, in power plants or from the atmosphere, is any-

the great promise of this option, intensive R&D efforts are being made across the world which are briefly reviewed in this paper. The review is specifically focused on four broad approaches to decarbonization being currently pursued:

where near economic feasibility. Worse, all options seem to be

frought with serious ecological and societal risks. Not the least of the challenge is associated with the overall magnitude of the

task: as much as 25 billion tonnes of CO2 is generated worldwide by anthropogenic activities every year [19] and all of it has to be

captured and safely sequestered if the globe is to be stopped from

getting warmer than it already has. As things stand, it will be quite

some time before truely eco-friendly as well as cost-effective decar-

bonization technologies are developed, if at all. Nevertheless, given

- (i) Capture and sequestration of CO2 before or after fossil fuel combustion
- (ii) Fossil fuel hydrogen production with CO<sub>2</sub> sequestration
- (iii) Direct decarbonization of fossil fuels by solid carbon capture
- (iv) Capture of atmospheric CO<sub>2</sub>

Various innovative ideas are being advanced for each of the broad approaches. Of these a few are under large-scale field-testing,

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for example CO<sub>2</sub> sequestration for an enhanced oil recovery [13,37], but most are still undergoing the preliminary proof-of the-concept scrutiny or technical feasibility assessment [15,38].

## 2. $CO_2$ capture and sequestration before or after fossil fuel combustion

2.1. In-plant carbon dioxide capture and sequestration (ICCS): pre-combustion and post-combustion capture of  $CO_2$  in power plants

In this route  $CO_2$  is sought to be captured and securely stored in geologic formations (e.g., deep coal seams, depleted oil and gas reservoirs), the ocean, saline aquifers, terrestrial ecosystems, etc. [31].

Two technological approaches are being pursued: precombustion or post-combustion (Fig. 1). In the former approach (Fig. 1A), the fossil fuel is reformed or gasified to a syngas (predominantly, a mixture of  $H_2$  and CO), which is further processed to  $H_2$ – $CO_2$  mixture. After capturing  $CO_2$  from the gas, hydrogen is used for power generation as a non-carbon fuel. In the other approach,  $CO_2$  is captured after combustion of a fossil fuel (e.g., from flue gases at power stations) using air (Fig. 1B) or oxygen (Fig. 1C). The advantage with using oxygen for combustion instead of air is that the flue gas doesn't get diluted with nitrogen, and consists mainly of water vapor and  $CO_2$ . After condensation of water, an almost pure  $CO_2$  stream results for sending to the sequestration unit.

One of the routes to precombustion decarbonization is the sorption-enhanced water-gas shift (SEWGS) process [38]. In this process carbon dioxide is removed from a synthesis gas at elevated temperature by adsorption. Simultaneously, carbon monoxide is converted to carbon dioxide by the water-gas shift reaction. The periodic adsorption and desorption of carbon dioxide is induced by a pressure swing cycle, and the cyclic capacity can be amplified by purging with steam. Among the sorbents, hydrotalcite-based materials have been found particularly attractive and commercial

high-temperature shift catalysts are utilizable for the conversion of carbon monoxide.

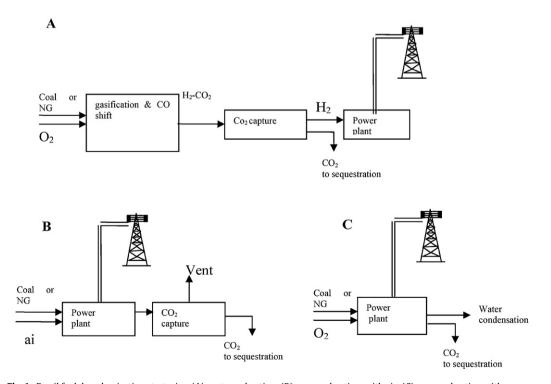
Even though, on surface ICCS appears to be a very attractive route to making the fossil fuel use a clean exercise, in practice ICCS is an energy-intensive and costly process involving several steps: CO<sub>2</sub> capture, pressurization, liquefaction, transportation and final disposal [34]. The last, and the most crucial of the three steps, which may involve injection of liquid CO<sub>2</sub> (L-CO<sub>2</sub>) into geologic formations, or in aquifers, is fought with major ecological and societal risks.

It has been estimated by the Intergovernmental Panel on Climate Change [19] that the addition of the ICCS provision to any power plant would increase the fuel usage by 11–40% and the cost of energy from a new power plant with CCS will go up by 21–91% [31]. Even partial reduction in carbon emissions to 112 g/kWh would increase the kwh cost by about 32% [15]. A carbon tax as high as \$100–300/tonne would be necessary to make CO<sub>2</sub> sequestration viable with the current technology [18]. The net cost of CO<sub>2</sub> disposal, however, could be significantly reduced if CO<sub>2</sub> sequestration is accompanied by an enhanced oil recovery [8], or if the power plant is located near depleted natural gas wells where recovered CO<sub>2</sub> could be re-injected. But such favorable sites are only few, and far between.

### 2.2. Storage/disposal of captured CO2

Capturing CO<sub>2</sub> is only half of the challenge; the more difficult half is to 'lock-away' the captured gas. The quantities involved are staggering, of the order of billions of tonnes per year. Some of the ongoing large-scale demonstration and field testing projects, mainly for CO<sub>2</sub> sequestration far an enhanced oil recovery, are:

 Deep saline aquifer disposal of CO<sub>2</sub> (about 1 million tonnes/year) captured from an offshore natural gas processing platform, at Norway.



**Fig. 1.** Fossil fuel decarbonization strategies: (A) post-combustion; (B) pre-combustion, with air; (C) pre-combustion with oxygen.

- Sequestration of over 28 million tonnes/year of CO<sub>2</sub> for an enhanced oil recovery, at USA.
- Enhanced gas recovery demonstration project of 8 million tonnes CO<sub>2</sub>/year capacity, at The Netherlands.
- A project in which 3 million tonnes of CO<sub>2</sub> per year is injected into a coal seam, European Union.
- Capture of 1.5 million tonnes CO<sub>2</sub> per year and piping it to Weyburn (Canada) for enhanced oil recovery, at USA/Canada.
- Capturing of CO<sub>2</sub> from natural gas (NG) processing and reinjection for enhanced NG recovery; 1.2 million tonnes CO<sub>2</sub>/year, at Algeria.
- Disposal of 0.1 million tonnes CO<sub>2</sub>/year in saline formation and a depleted gas field, at Australia.
- Capture of 0.01 million tonnes of CO<sub>2</sub> per year and disposal in a deep land-based saline formation, European Union.

Implementation of these technologies on a large-scale world-wide as a solution for the fossil fuel-related environmental problems would become feasible only if three major challenges are overcome [16]:

- (i) Significant reduction in cost.
- (ii) An assessment of key risk factors associated with the long term environmental impact.
- (iii) Finding adequate sinks or 'storehouses' for the captured CO<sub>2</sub>.

Deep ocean CO<sub>2</sub> sequestration has been proposed but it has more opponents than advocates because of its possibly very serious impact on the aquatic environment in the form of ocean acidification and other major disruptions in the marine and oceanic life. As it is, oceans have come under serious threat due to the acidification that has already occurred [5,26,33] as a consequence of having absorbed nearly a third of all extra CO<sub>2</sub> that has been emitted in the last 200 years. If oceans are forced to absorb more CO<sub>2</sub> the consequences can be catastrophic [11].

Geological disposal seems to be a less expensive option than ocean sequestration, but it has major hazards associated with it. For example, leakage of  $CO_2$  from the storage site could lower the pH of water-bodies causing the leaching of harmful trace elements in freshwater aquifers and can adversely affect soil chemistry [6]. It can also exacerbate the adverse impact of acid rain [2–4], thus compounding the associated risks [1,20–25]. Although  $CO_2$  injection into geologic formations is being practiced by petroleum industry for an enhanced oil recovery [8], it is not yet possible to predict with confidence the storage volumes, formation integrity and storage permanence over long time periods.

It would not be easy to find safe and secure spaces for storing the 25 billion tonnes of CO<sub>2</sub> produced annually worldwide. When such sites are located, it will not suffice to just assess the capacity of each prospective storage site but the probability of CO2 leaking from it over a reasonable period of time will also have to be assessed. Two classes of risks must be considered for CO2 storage sites: gradual and sudden [35]. The gradual risk includes 'domino effect' whereby one adverse impact becomes the trigger for another adverse impact which, in turn, propagate the impact chain further and further [21,24,25]. According to some estimates, even 1% leak rate could cancel out the sequestration effort in a century [10]. On the other hand, a sudden leakage could be catastrophic for humans and animals, considering potentially high human risk of a sudden CO<sub>2</sub> release. At the site of the lake Nahos in Africa, about three thousand people were asphyxiated when there was an abrupt release of CO<sub>2</sub> [31]. Given this antecedent, there will always be strong popular opposition to the location of CO<sub>2</sub> storage sites anywhere close to populated areas.

Another major concern is that the CCS route described above is technically feasible only for centralized sources, such as power plants, and large chemical plants. But those sources account for only about a half of the total CO<sub>2</sub> emissions to the atmosphere [19], and another half comes from domestic heat sources and transportation involving myriads of small dispersed sources of CO<sub>2</sub> that would be technically and economically prohibitive to capture and dispose. Taking all the above facts into consideration, it has been estimated that realistically only 20–40% of CO<sub>2</sub> emissions could be sequestered by 2050, which may prove 'too little too late' to prevent seriously adverse impact on climate [29].

### 2.2.1. Other avenues of CO<sub>2</sub> sequestration

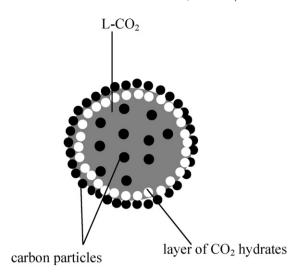
The environmental and direct human safety risks associated with geologic and ocean  $CO_2$  sequestration have prompted efforts to seek more environmentally 'benign' means of  $CO_2$  sequestration. Attempts are being made to develop methods with which permanent containment of the disposed  $CO_2$  can be achieved while avoiding negative environmental impact of the sequestration. Mineral carbonation is considered as a possible route: for example, the mineral olivine ( $Mg_2SiO_4$ ) can be used to convert  $CO_2$  into an environmentally benign mineral magnesite ( $MgCO_3$ ). It has also been proposed to mix liquid  $CO_2$  ( $L-CO_2$ ) with pulverized limestone and water and release the resulting emulsion in the oceans at a depth below  $500 \, \text{m}$  [17]. When  $L-CO_2$  is mixed with  $CaCO_3$  and water, the following equilibrium is established:

$$CO_2(1) + CaCO_3(S) + H_2O(1) \leftrightarrow Ca^{2+}(aq) + 2HCO_3^{-}(aq)$$
 (1)

The reaction lifts the pH around the release point by about 2 units, which is close to the ambient pH value. According to the proposers of this option, the bi-carbonate solution will have an indefinite sequestration time. But these  $\rm CO_2$  sequestration methods are prohibitively expensive and would increase the cost of  $\rm CO_2$  disposal in the ocean by 150%. Moreover oceanic disposal of large quantities of  $\rm CO_2$  in this manner is fraught with great risks mentioned earlier.

Among other ideas is the possible use of micron-sized carbon particles to stabilize L-CO<sub>2</sub> on the ocean floor by creating a protective carbon-CO<sub>2</sub>-hydrate 'skin' that would prevent L-CO<sub>2</sub> from interacting with seawater and, subsequently, changing its pH [30]. At the pressure of 100 bar and higher at the ocean floor and at the temperature prevailing there, L-CO<sub>2</sub> and water are not miscible, and the two liquids may remain separated into two phases similar to an oil-water system. The proposed concept is based on the assumption that if the L-CO<sub>2</sub>-water system indeed behaves like a two-phase oil-water system, it could be stabilized by micron-sized carbon particles in the same way as stabilization of oil-water emulsions by a film of highly dispersed solid particles occurs during the production of crude oil. In addition, the presence of polar groups on the surface of carbon particles could catalyze (or enhance) the formation of solid  $CO_2$  hydrates  $(CO_2 \cdot nH_2O, where 6 < n < 8)$  that would form a layer between seawater, carbon particles and L-CO<sub>2</sub> phase. If this happens, L-CO<sub>2</sub> will be protected by a double 'skin' of two solid phase layers: Carbon and CO2-hydrate (Fig. 2). Computer simulations indicate that the CO<sub>2</sub>-hydrate layer retards the CO<sub>2</sub> dissolution rate in water by a factor of 2.7 [12]. The presence of an additional carbon layer, in all likelihood, would further slow down the dissolution process.

In order for the  $CO_2$  droplet to sink at the depth of 500 m (where seawater density is  $1.027 \, g/mL$ ), the carbon:L- $CO_2$  ratio should be 1:9 (by weight) or greater. At the seawater depths of 500 m and greater, the  $CO_2$  hydrate has the density  $1.12 \, g/mL$ , i.e., about 10% greater than seawater, which would allow significantly reducing the amount of carbon required to sink the carbon: L- $CO_2$  droplet. Further, it would suffice to inject the carbon-laden L- $CO_2$  droplets at the depth of 500 m, instead of 3000 m that would be required for L- $CO_2$  injection without carbon. This would substantially lower the cost of  $CO_2$  sequestration by reducing the length of pipelines



**Fig. 2.** Representation of the formation of a double layer of hydrates (white bullets) and carbon (block bullets) around liquid CO<sub>2</sub> droplet.

and decreasing the energy consumption. It would also increase the number of sites along the coastline that could be used for  ${\rm CO_2}$  sequestration.

Very preliminary 'proof-of-the-concept', experiments using silicone oil (density 0.971 g/mL) as a L-CO<sub>2</sub> model have demonstrated that the oil droplets with suspended carbon black particles sank to the bottom of a beaker filled with seawater, and the resulting carbon-oil-seawater system was stable for over 15 months. But the proposed concept would be technically and economically viable only if large quantities of carbon are available; from this viewpoint any carbonaceous material, including coal particles, natural carbonates, petroleum coke, etc. could potentially be applicable.

But whether the above-mentioned approaches to sequester  $\mathrm{CO}_2$  will really be environmentally benign? This question cannot be answered in the affirmative unless sufficiently large-scale and long duration tests are performed. A vast amount of fundamental and applied research and field-testing will be needed before the economic viability and environment-friendliness of these  $\mathrm{CO}_2$  disposal methods are established.

# 3. Generating hydrogen from fossil fuels with simultaneous CO<sub>2</sub> sequestration

This strategy revolves round generation of hydrogen from natural gas, petroleum or coal, coupled with CO<sub>2</sub> sequestration (Winter, 2009). According to this strategy, chemical energy of a fossil fuel is converted to chemical energy of hydrogen, and CO2, which is a byproduct, is captured and sequestered (thus preventing it from reaching the atmosphere). In the case of coal as a feed, the hydrogen that is generated almost entirely comes from the water used in the reaction (with the energy conversion efficiency of 50–60%), while, in the case of natural gas (NG), half of hydrogen comes from water and another half from NG (with the energy conversion efficiency of 70–75%). The charm of this approach is that even as it is based on the energy infrastructure of carbonaceous fuels, it actually generates and utilizes an ecologically clean fuel, i.e. hydrogen, in the bargain. The present NG reserves are sufficient to support the hydrogen fuel initiative for several decades. It has been projected that by 2040 the annual production of hydrogen would be about 150 million tonnes, and it may replace 18.3 million barrels/day of petroleum provided that, by that time, the hydrogen fuel cell vehicles have been made 2.5 times more efficient than gasoline cars [9].

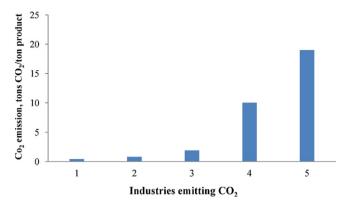


Fig. 3. Comparison of CO<sub>2</sub> emissions from different industrial sources.

The strategy of hydrogen production coupled with  $\mathrm{CO}_2$  sequestration has been advocated by a number of research groups worldwide with a special emphasis on steam methane reforming (SMR) as the technology of choice for production of hydrogen [7]. SMR is by far the most widely used process for the industrial manufacture of hydrogen, amounting to about 80% of the hydrogen produced in USA. The remaining 20% is a byproduct of chemical processes such as chlor-alkali production. In contrast, water electrolysis represents only a small fraction of the emergant hydrogen market. The SMR process can be expressed by the equation:

$$CH_4 + 2H_2O(1) \rightarrow 4H_2 + CO_2 \quad \Delta H^\circ = 253 : 1 \text{ kJ/mol}$$
 (2)

The technology for SMR is well developed and is applicable to a wide range of scales, from less than one tonne/h  $H_2$  (small decentralized units) to about 100 tonnes/h  $H_2$  (large ammonia manufacturing plants). The global warming potential (GWP) of hydrogen production via the SMR process is  $13.7\,\mathrm{kg}$  CO $_2$  (equivalent) per kg of net hydrogen produced. This calculation assumes that CO $_2$  accounts for 77.6% of the system's GWP, which is defined as a combination of  $\mathrm{CO}_2$ ,  $\mathrm{CH}_4$  and  $\mathrm{N}_2\mathrm{O}$  emissions expressed as  $\mathrm{CO}_2$  equivalence for a 100 year timeframe [36]. Thus, a typical SMR hydrogen plant with the capacity of one million standard cubic meters of hydrogen per day produces over  $0.4\,\mathrm{million}\,\mathrm{m}^3/\mathrm{day}$  of  $\mathrm{CO}_2$ . This rate of  $\mathrm{CO}_2$  generation is very high, more than even the  $\mathrm{CO}_2$  emissions (per unit of product) from some highly polluting industries (Fig. 3). Hence the necessity to capture and sequester  $\mathrm{CO}_2$  if SMR technology has to be made 'clean'.

The economics of hydrogen production by SMR process with CO<sub>2</sub> capture and disposal in a saline aquifer has been assessed [12]. It has been estimated that this would add about 25–30% to the cost of hydrogen production. The costs of avoiding CO<sub>2</sub> emissions would be about US\$20 (about Rs 900) per tonne of CO<sub>2</sub> avoided. The U.S. National Research Council (NRC) estimates that the cost of centralized hydrogen production by SMR with added CO<sub>2</sub> sequestration would be about 18.5% higher than the cost without CO<sub>2</sub> capture [32].

The possibility of decentralized (or distributed) production of hydrogen (e.g., on-site SMR reformers at gas-filling stations) has also been considered but the cost of CO<sub>2</sub> capture and sequestration associated with distributed hydrogen production is prohibitive. Another major worry about the SMR process is that increased production of hydrogen by SMR will jack up the demand for NG and what is an oil insecurity problem at present may transform to an NG insecurity problem. As the resources of light hydrocarbon fuels (NG, liquefied petroleum gas, naphtha) will gradually dwindle, heavier carbonaceous feed stocks such as heavy oil, oil shale, tar sands and coal, would have to be used in production of hydrogen. However, these feed stocks have significantly higher carbon-to-hydrogen ratio than NG, and, thus, would produce about

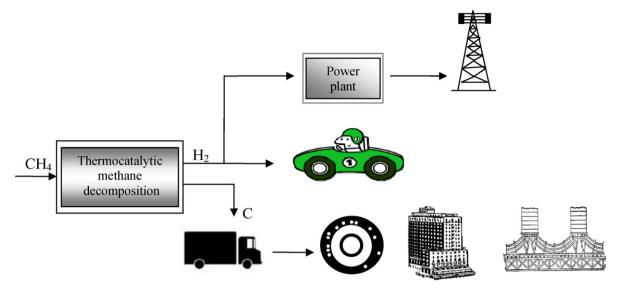


Fig. 4. The direct decarbonization concept.

Adopted from [31].

twice as much CO<sub>2</sub> emission per unit of hydrogen production [34], thereby enhancing the quantities of CO<sub>2</sub> to be captured and sequestrated per unit mass of hydrogen production. These feed stocks also contain various impurities, e.g., sulfur, nitrogen, mercury, etc., that would significantly complicate the gasification and purification processes. The oil shale deposits found in the U.S. (the states of Colorado, Wyoming and Utah) are among the largest in the world; the oil contained in these deposits is estimated at about 1.5-1.8 trillion barrels of recoverable shale oil, sufficient to meet U.S. consumption for several centuries. Likewise, the vast resources of coal in U.S. could potentially last for about 250 years if consumed at the current consumption rate. Driven by the possibility of utilizing all this fuel, the development of advanced gasification technologies for the production of syngas and hydrogen is being attempted vigorously [37]. However, success of such attempts squarely depends on the development of cost-effective and environmentally safe methods for sequestering billion of tonnes of CO<sub>2</sub> per year. Given the past experience with all major authropogenic activities, there are always unforeseen impacts which show up in most unexpected ways - as acid rain, ozone hole, and global warming have - and 'environmentally benign' sequentration of massive quantities of CO<sub>2</sub> may never be possible.

# 4. Direct decarbonization of fossil fuels with solid carbon capture

Avenues are also being explored to decarbonize fossil fuels by recovering and sequestering solid carbon instead of gaseous CO<sub>2</sub> [14,27,31]. This initiative is based on effecting dissociation of hydrocarbons to hydrogen and elemental carbon in an air—water free environment. It is generally referred to as 'direct decarbonization', since it involves direct extraction of carbon from fossil fuels. Since methane (as NG) is the most preferred feedstock for the present-day and, in all likelihood, near-future production of hydrogen, this discussion would centre around the decarbonization of methane although the concept is applicable to any gaseous or even liquid hydrocarbon fuel.

Decarbonization of methane occurs as follows:

$$CH_4 \rightarrow C + 2H_2 \quad \Delta H^{\circ} = 75 : 6 \text{ kJ/mol}$$
 (3)

This reaction is moderately endothermic, and the energy requirement per mole of hydrogen produced (37.8 kJ/mol H<sub>2</sub>)

is considerably less than that for the steam reforming process (63.3 kJ/mol H<sub>2</sub>). Hydrogen produced in the process (Fig. 4) can be used as a carbon-free energy carrier, e.g., a fuel for transportation and power generation. The other product – carbon – can be utilized in a variety of traditional and novel ways. It can also be stored (or sequestered) in a more safe manner than is possible with CO<sub>2</sub>. Although the methane decomposition reaction seems to produce only half as much hydrogen as the SMR reaction, it uses less methane than the strongly endothermic SMR process and if the energy loses due to CO<sub>2</sub> sequestration are considered, the overall energy efficiencies for the SMR and methane decomposition processes become comparable (60 and 58%, respectively). Moreover, in the latter option, the chemical energy of the product (carbon) is not lost, but is stored away for possible future use.

The major problem with the methane dissociation reaction is that methane is one of the most stable organic molecules, due to its strong C-H bonds ( $E_{\rm dis}$  = 436 kJ/mol) and the lack of polarity. The reaction (3) requires an energy input in the form of very hightemperature (>1200 °C) heat or electrical discharge (or plasma). There are several technological options for methane dissociation to hydrogen and carbon, which are summarized in Fig. 5. Of these, thermal decomposition has been practiced since 1930s for production of carbon black (with hydrogen as byproduct which also becomes a supplementary fuel). A Norwegian company has developed and operated on a limited commercial scale a thermal plasma process for decomposition of methane and other hydrocarbon feedstocks to hydrogen and carbon black. Although technologically simple, the process is energy intensive: It was estimated that up to 1.9 kWh of electricity is consumed for each cubic meter of hydrogen produced [31].

The temperature needed for methane dissociation can be reduced by the use of catalysts. Metal based and carbon based catalysts have been developed for the use in thermo-catalytic decomposition (TCD) of methane. Of these, metallic catalysts have been most commonly used for the TCD process but they suffer from deactivation problem associated with carbon build up on the catalyst surface. In some processes, the catalyst is regenerated by combustion of carbon (which also provides heat input to the process), but this results in considerable CO<sub>2</sub> emissions. Another serious problem arising from the oxidative regeneration of metal catalysts relates to unavoidable contamination of hydrogen with carbon oxides, which would require an additional purification step.

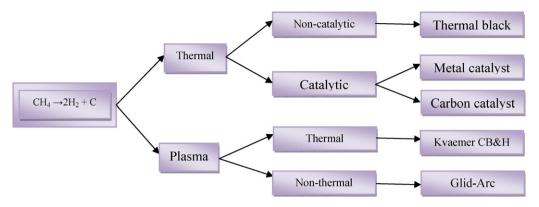


Fig. 5. Various pathways for the decomposition of methane to hydrogen and carbon.

At optimal operational conditions, high-value filamentous carbon (or multi-wall carbon nanotubes) could also be produced as a product of the metal-catalyzed methane decomposition process.

In contrast to metal-based catalysts, carbon catalysts are resistant to sulfur and temperature. It has been shown that efficient catalytic methane decomposition can be accomplished over high surface area disordered carbons at the temperatures typical of the SMR process (800-900 °C). X-ray diffraction (XRD) studies of carbon catalysts indicate that after their exposure to hydrocarbons, the 'columnar' or stacking direction gets more ordered than before. Thus, carbons produced by decomposition of methane or propane have a more ordered structure compared to amorphous carbon, but they are less structurally ordered than graphite (which is characteristic of the so-called turbostratic carbon). Novel active and stable catalysts for metal- and carbon-catalyzed decomposition of methane and light hydrocarbons into hydrogen and value added carbon products have to be developed if the efficiency and sustainability of the TCD process has to be improved and its commercial potential is to be enhanced.

Techno-economic evaluation of methane TCD indicates that the hydrogen production cost is a function of the selling price of the carbon that is produced. The carbon produced in the carbon-catalyzed methane decomposition process is a sulfur and ash-free product that could be marketed at good selling price. At the same time, it must be noted that the annual worldwide consumption of all carbon products amounts to only 15–20 million tonnes, which is much lesser than the quantities of carbon that would be generated if reasonable quantities of hydrogen were to be produced via methane TCD. Hence the gain from carbon selling would, infact, be rather limited unless new avenues of carbon use open up.

Among the prospects of increased carbon use is in the building and construction materials. Traditional construction materials can be substituted for advanced carbon-based materials, e.g., carbon-carbon composites, manufactured graphites, etc. Carbon fiber composites are used for some of the automotive parts and components where the need for special properties of weight and strength outweigh cost considerations. The next generation of commercial airliners under development by Boeing and Airbus is expected to make extensive use of carbon fiber composite construction. The advantages of using carbon composites over traditional materials (e.g., steel) are that they do not corrode, are 5 times lighter than steel, and can be installed without the use of heavy construction equipment.

In recent years, there has been an increasing attention focused on environmental impact of the concrete usage. Concrete is the most dominant construction material (60% of the entire infrastructure) with the worldwide annual production capacity of 5 billion tonnes, requiring close to 1.5 billion tonnes of cement [28]. Cement industry generates immense amounts of CO<sub>2</sub> emissions (on an aver-

age, one tonne of  $CO_2$  per tonne of cement). There is a global effort aimed at developing alternatives to concrete that are more sustainable and environment friendly. The replacement of concrete with carbon materials would result in huge reductions in overall  $CO_2$  emissions due to phasing out of cement manufacturing plants. Recent developments show a great potential of using carbon-based products as additives and, eventually, substitutes for cement.

It may also become feasible to utilize the carbon products of methane decomposition for manufacturing of structural carbon materials (similar to commercial carbon composites and manufactured graphites) that could potentially replace concrete. Manufactured graphites and other commercial carbon composite materials are made by mixing petroleum coke particles with a binder-pitch. Similar products could be produced from the carbon obtained in methane decomposition by binding it with low cost and abundant byproduct of oil refining: petroleum pitch. Carbon particles produced by carbon-catalyzed decomposition of methane exhibit semidisordered (turbostratic) structure, and in many respects are similar to petroleum coke particles, but much cleaner, since they do not include sulfur, heavy metals and other impurities. The hardness of TCD-produced carbon particles is between that of graphite and diamond. NG-derived carbon filaments and turbostratic carbon particles have been formed into carbon bricks (using petroleum pitch as a binder) that show a mechanical strength close to that of commercial composite materials.

### References

- Abbasi SA, Abbasi N. The likely adverse environmental impacts of renewable energy sources. Applied Energy 2000;65:121–44.
- [2] Abbasi T, Kannadasan T, Abbasi SA. Impact of acid rain on chromium toxicity. International Journal of Environmental Studies 2009;66:765–71.
- [3] Abbasi SA, Soni R. Stress-induced enhancement of reproduction in earthworm Octochaetus pattoni exposed to chromium (VI) and mercury (II)—implications in environmental management. International Journal of Environmental Studies 1983;22:43–7.
- [4] Abbasi SA, Soni R. Teratogenic effects of chromium (VI) in environment as evidenced by the impact on larvae of amphibian Rana tigrina: implications in the environmental management of chromium. International Journal of Environmental Studies 1984;23:131–7.
- [5] Abbasi T, Abbasi SA. Ocean acidification—the newest threat to global environment. Critical Reviews in Environment Science & Technology; in press.
- [6] Abbasi SA. Extraction and spectrophotometric determination of vanadium (V) with N-[p-N,N-dimethylanilino-3-methoxy-2-naphtho]hydroxamic acid. Analytical Chemistry 1976;4:714-7.
- [7] Audus H, Kaarstad O, Kowal M. Decarbonization of fossil fuels: hydrogen as an energy carrier. In: Proceedings of the XI world hydrogen energy conference. 1996.
- [8] Ayatollahi S, Tauseef SM, Guzman C. Compositional model optimizes gas lift. Oil & Gas Journal 2005;102:37–42.
- [9] Cameron DS. Fuel cells science and technology 2008. Platinum Metals Review 2009;53:147–54.
- [10] DOE. Basic research needs for solar energy utilization. Report of the US Department of Energy Basic Energy Sciences Workshop on Solar Energy Utilization. Publ. Argonne Nat. Lab; 2005.

- [11] Doney SC, Fabry VJ, Feely RA, Kleypas JA. Ocean acidification: the other CO<sub>2</sub> problem. Annual Review of Marine Science 2009;1:169–92.
- [12] Fer I, Haugan P. Dissolution from a liquid CO2 lake disposed in the deep ocean. Limnology and Oceanography 2003;48:872–83.
- [13] Flavin C. Low-carbon energy: a roadmap. In: Worldwatch Paper; 2008. p. 1-49.
- [14] Fulcheri L, Schwob Y. From methane to hydrogen, carbon black and water. International Journal of Hydrogen Energy 1995;20:197.
- [15] Gambini M, Vellini M. CO<sub>2</sub> emission abatement in CC-IGCC power plants: energy and economic comparisons. ASME International Mechanical Engineering Congress and Exposition, Proceedings 2009;8:247–61.
- [16] Gambini M, Vellini M. Hydrogen use in an urban district: environmental impacts in a possible scenario based on coal. In: ASME International Mechanical Engineering Congress and Exposition, Proceedings, 8. 2009. p. 611–25.
- [17] Golomb D, Angelopoulos A. A benign form of CO<sub>2</sub> sequestration in the ocean. In: DOE NETL workshop on carbon sequestration science. 2001.
- [18] Herzog H. CO<sub>2</sub> sequestration. In: Slott R, editor. Proceedings of greenhouse gas reduction programs and technologies symposium. 2002. p. 11–2.
- [19] IPCC. Intergovernmental panel on climate change. Fourth assessment report. Paris: Working Group III; 2007.
- [20] Khan FI, Abbasi SA. Accident hazard index: a multi-attribute method for process industry hazard rating. Process Safety and Environmental Protection 1997:75:217-24.
- [21] Khan FI, Abbasi SA. Inherently safer design based on rapid risk analysis. Journal of Loss Prevention in the Process Industries 1998;11:361–72.
- [22] Khan FI, Abbasi SA. Assessment of risks posed by chemical industries—application of a new computer automated tool MAXCRED-III. Journal of Loss Prevention in the Process Industries 1999;12: 455–69
- [23] Khan FI, Abbasi SA. Analytical simulation and PROFAT II: A new methodology and a computer automated tool for fault tree analysis in chemical process industries. Journal of Hazardous Materials 2000;75:1–27.
- [24] Khan FI, Abbasi SA. Risk analysis of a typical chemical industry using ORA procedure. Journal of Loss Prevention in the Process Industries 2000;14: 43–59.

- [25] Khan FI, Abbasi SA. Risk analysis of an epichlorohydrin manufacturing industry using the new computer automated tool MAXCRED. Journal of Loss Prevention in the Process Industries 1997:10:91–100.
- [26] Kleypas JA, Feely RA, Fabry VJ. Impacts of ocean acidification on coral reefs and other marine calcifiers: a guide for future research. St. Pertsburg, FL, USA; 2006, p. 88
- [27] Lynum S, Hildrum R, Hox K, Huglahl J. Kværner based technologies for environmentally friendly energy and hydrogen production. In: Proceedings of the 12th world hydrogen energy conference. 1998.
- [28] Mak S. Where are construction materials headed; 2003. www.dbce.csiro.au/inno-web/0899/sustainable.htm.
- [29] Moriarty P, Honnery D. Intermittent renewable energy: the only future source of hydrogen? International Journal of Hydrogen Energy 2007;32:1616–24.
- [30] Muradov N. Role of carbon in environmentally "benign" sequestration of CO<sub>2</sub>. In: Proceedings of the XVII World Hydrogen Energy Conference. 2008.
- [31] Muradova NZ, Veziroglu TN. "Green" path from fossil-based to hydrogen economy: an overview of carbon-neutral technologies. International Journal of Hydrogen Energy 2008;33:6804–39.
- [32] NRC (National Research Council). The hydrogen economy. Opportunities, costs, barriers and R&D needs. Washington, DC: National Academies Press; 2004.
- [33] Raven J, Caldeira K, Elderfield H. Ocean acidification due to increasing atmospheric carbon dioxide. London: Royal Society; 2005.
- [34] Shinnar R, Citro F. Decarbonization: achieving near-total energy independence and near-total elimination of greenhouse emissions with available technologies. Technology in Society 2008;30:1–16.
- [35] Sokolow R. Can we bury global warming? Scientific American 2005:49–55.
- [36] Spath P, Mann M. Life cycle assessment of hydrogen production via natural gas steam reforming. Technical Report, NREL, NREL/TP-570-27637; 2000.
- [37] Steinberg M. From Manhattan project to global warming the science and technology of CO2 mitigation. In: TMS annual meeting, 2008. p. 3–18.
- [38] van Selow ER, Cobden PD, Verbraeken PA, Hufton JR, Van Den Brink RW. Carbon capture by sorption-enhanced water-gas shift reaction process using hydrotalcite-based material. Industrial and Engineering Chemistry Research 2009;48:4184–93.